2017 International Nuclear Atlantic Conference - INAC 2017
Belo Horizonte, MG, Brazil, October 22-27, 2017
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR – ABEN

Agência Brasileira do ISBN
ISBN 978-85-99141-07-6

DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN SEDIMENT SAMPLES OF BRAZILIAN MULTIPURPOSE REACTOR (RMB) INSTALLATION AREA

Juliana C. Silva, Elâine A. J. Martins, Marycel E. B. Cotrim and Maria A. F. Pires

Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
jcsilva@usp.br

elaine@ipen.br

mecotrim@ipen.br

mapires@ipen.br

ABSTRACT

RMB will be a nuclear reactor for research and production of radioisotopes. Its applications extend to agriculture, industry and the environment. With the changes that will occur in the study area by its construction, the flow of vehicles will increase. It is known that one of the largest anthropogenic sources of PAHs is from the burning of fossil fuels and biomass. The aim of this research was to identify and quantify 14 of the 16 majorities PAHs in the sediment samples at RMB installations area in a period before the enterprise construction, June 2017, using the methodology developed and validated by Brito, 2009. It was observed individual concentrations from 0.05 to 1.11 µg g^{-1} in this first evaluation indicating that, although were found some PAHs concentrations above the established values by CONAMA and CETESB, this area still remains preserved. Pyrene was the compound that had the highest concentrations at different collecting points (1.11±0.03 and 1.09±0.02 µg g^{-1}). Although were observed some PAHs concentrations above the established values by CONAMA and CETESB, the area is preserved. The study will provide previous information on PAHs concentrations in the area of the enterprise, providing information for the environmental impact study after the construction of the enterprise.

1. INTRODUCTION

Environment protection is a subject that has become increasingly important in the society in which we live, which has required fast and efficient mechanisms to control environment contamination [1].

One of the factors that contributed most to the increase of environment contamination was population growth over the last few centuries, with increased demand for natural resources, available, energy and matter, loss of biodiversity, increased emissions of gases that pollute not only the atmosphere, but also water and soil due to anthropogenic waste [2].

The scientific community has turned its attention to human exposure to compounds that even in low concentrations, moderate but continuous doses have toxic effects. Contamination by phenolic micropollutants in aquatic environments has been studied due to the imbalance they cause, damaging the functionality of the environment and water quality, especially those used for human consumption [1; 3-4].

Sediment is one of the most important compartments of the aquatic ecosystem, because physical, chemical and biological processes occur in it. Due its direct interaction with water column and because it is a compartment where the low solubility compounds are deposited, the sediments are used for evaluation studies of the pollution of a water body and its quality, since pollutants interact between water and sediment [5].

The main sources of pollutants that are released into the atmosphere are from anthropogenic activities and are usually in the form of particulate matter or gases that are eventually transported to the ground due to precipitation. When the pollutants reach the soil, it is carried to the bodies of water and subsequently deposited in the sediments surface that is the final destination of the pollutants [2-3].

Polycyclic Aromatic Hydrocarbons (PAHs) are organic pollutants formed from incomplete combustion of carbonaceous materials at high temperatures. The main sources of emissions are the burning of fossil fuels and biomass. These pollutants have two or more aromatic rings condensed in its carbon and hydrogen structure [6].

Some of these compounds are considered as potentially carcinogenic, teratogenic and mutagenic. PAHs have low solubility in water, are thermolabile and hydrophobic, but are highly lipophilic and soluble in most organic solvents. They tend to be associated with particulate matter, soil and sediment. They can be degraded by some fungi and microorganisms present in the soil. Because they are lipophilic, PAHs are easily permeated by biological membranes, and it is possible to detect low Benzo[a]Pyrene levels in most tissues within minutes to hours after exposure [6].

The population may be exposed to PAHs from a variety of sources, such as air, inhalation, dermal contact and inhalation of soil resuspended particles and dust, or by food and water consumption [7].

Several studies on drinking water in the USA reported carcinogenicity values of PAHs in the range of 0.1 to 61.6 ng L^{-1} [7-8]. In many cities in Europe and Canada, the concentration range of the 16 major PAHs was 106.5 to 150.3 ng.L^{-1} [9]. In Taiwan and China, the found values were lower, in the range of 85.2 to 94.6 ng.L^{-1} [10]. Table 1 shows some characteristics of the 14 PAHs studied in this research.

Table 1: Physicochemical properties of 14 PAHs studied.

Compound	**Molecular formula**	**Melting point (ºC)**	**Boiling point (ºC)**	**Solubility in water (mg L^{-1}) at 25ºC**
Acenaphthylene	C12H8	89.4	280	3.93
Fluorene	C13H10	114.8	294	1.69
Acenaphthene	C12H10	93	297	3.9
Phenanthrene	C14H10	101	340	1.15
Anthracene	C14H10	218	339.9	1.29
Fluoranthene	C16H10	110.2	384	0.26
Pyrene	C16H10	150.4	393	0.14
Benzo[a]anthracene	C18H12	162	437	0.009
Chrysene	C18H12	255	448	0.002
Benzo[b]fluoranthene	C20H12	168	481	0.0015
Benzo[k]fluoranthene	C20H12	217	480	0.0008
Benzo[a]pyrene	C20H12	179	496	0.0038
Dibenzo[a,h]anthracene	C22H14	269	524	0.0006
Indene[1,2,3-cd]pyrene	C22H12	164	536	0.0006

Source: Modified from WHO [6].

Of the cases of environmental contamination registered in the State of São Paulo up to the year 2010, about 1411 were due to PAHs, losing only to cases of liquid fuels (2431) and aromatic solvents (2339), as it can be observed in Figure 1.

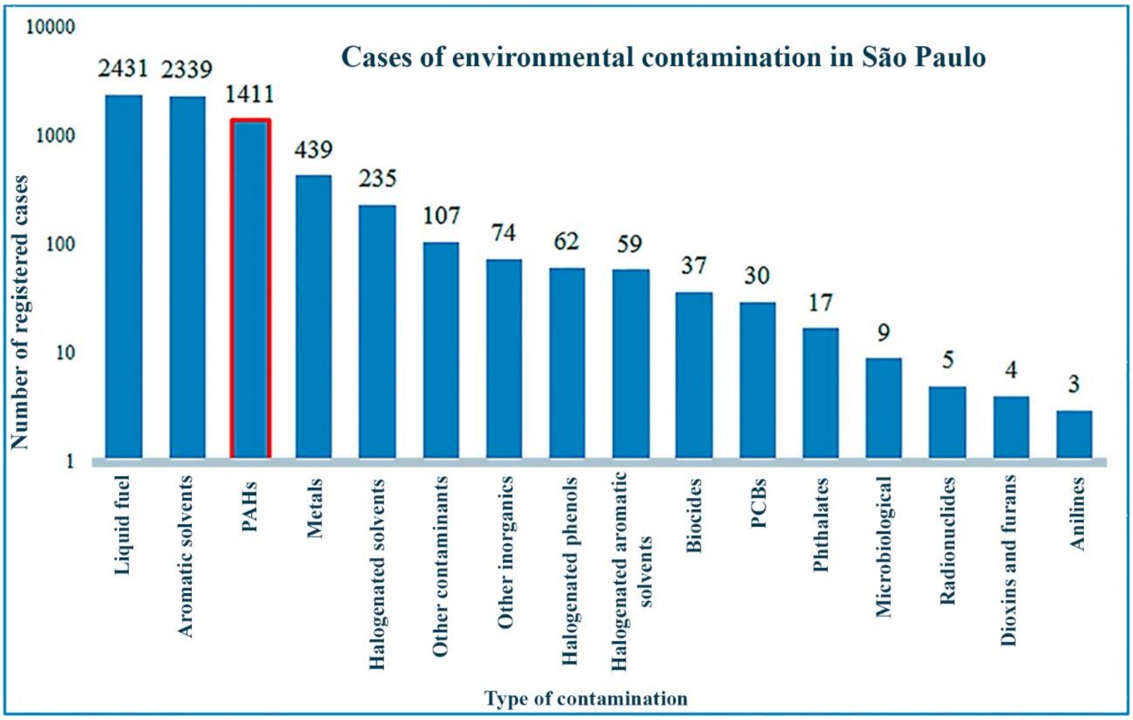

Figure 1: Contaminants in the São Paulo state [11].

Most organic pollutants (including PAHs) that are released daily into water bodies are not covered by Brazilian legislation. In addition, there are currently no legislations for the sediment matrix, only guiding values (Table 2) that contribute to decision-making for these compounds while there is no legislation pertinent to the sediment matrix [11-12].

Table 2: Guiding values to soil and subterranean water

Compounds	Soil (mg kg^{-1} of dry weight							
	Prevention (CETESB, 2014)	Prevention (CONAMA, 2009)	Investigation					
			Agricultural (CETESB, 2014)	Agricultural (CONAMA, 2009)	Residential (CETESB, 2014)	Residential (CONAMA, 2009)	Industrial (CETESB, 2014)	Industrial (CONAMA, 2009)
Polycyclic Aromatic Hydrocarbons								
Anthracene	0.3	0.039	2300	-	4600	-	10000	-
Benzo[a]anthracene	0.2	0.025	1.6	9	7	20	22	65
Benzo[b]fluoranthene	0.7	-	2	-	7.2	-	25	-
Benzo[k]fluoranthene	0.8	0.38	27	-	75	-	240	-
Benzo[g,h,i]perilene	0.5	0.57	-	-	-	-	-	-
Benzo[a]ýrene	0.1	0.052	0.2	0.4	0.8	1.5	2.7	3.5
Chrysene	1.6	8.1	95	-	600	-	1600	-
Dibenzo[a,h]antrracene	0.2	0.08	0.3	0.15	0.8	0.6	2.7	1.3
Phenanthrene	3.6	3.3	15	15	40	40	95	95
Indene[1,2,3-c,d]pyrene	0.4	0.031	3.4	2	8	25	30	130

Source: adapted from CETESB; CONAMA[11-12]

The main objective of this research is to determine the concentration of 14 of the 16 major PAHs (Acenaphthylene, Fluorene, Acenaphthene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo[a]anthracene, Chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Dibenzo[a,h]anthracene and Indene[1,2,3-c, d]pyrene) that may be present in the sediment samples collected from the water bodies of the installation area of the Brazilian Multipurpose Reactor (RMB) in order to promote a monitoring of the environmental impact that the construction of the undertaking may cause.

2. MATERIALS AND METHODS

2.1. Study Area

The installation area of the Brazilian Multipurpose Reactor–RMB (23º23’33,5”S 47º37’12,4”W) is located in the municipality of Iperó, approximately 125 km away from São Paulo city. The chosen study area is part of the Tietê/Sorocaba Water Resources Management Unit (UGRHI–10), in the Sorocaba River Hydrographic Basin. The site (Figure 2) is a plateau at 580 m above sea level, covering approximately 2.054 million m^2 in rural area, where 1.214 million m^2 were ceded by Technological Center of the Navy (CTMSP), and the other 840 thousand m^2 were ceded by the State of São Paulo to Comissão Nacional de Energia Nuclear (CNEN). The nearest urban area is approximately 7 km away from the RMB.

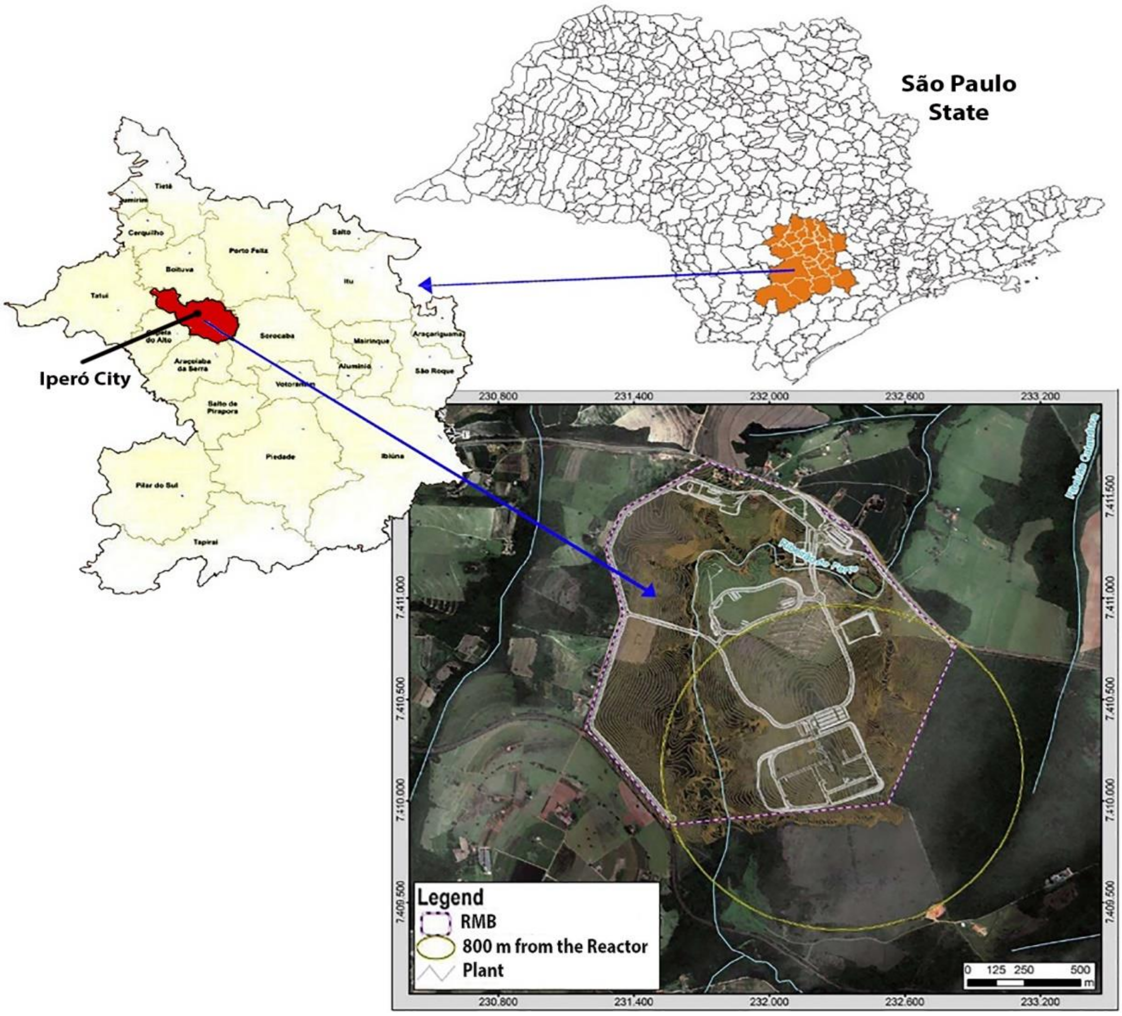

Figure 2: Location of RMB.

2.2. Sampling

The sediment sample collections occurred in June 2017, in a very rainy season. Were defined, according to Table 3 and Figure 3, four sampling points, the same as the RMB-PMRA Pre-Operational Environmental Radiological Monitoring Program, inside the study area within a 15 km radius, including the surrounding area.

Table 3: Descriptions of sediment's collection points.

ID do ponto	Localização	Latitude e Longitude
PC2	Ribeirão do Ferro, upstream of the RMB	23º17'25" S 74º09"219"W
P6 (PAS1)	Ribeirão do Ferro, downstream of the RMB	23º25'23" S 74º11'043"W
P7 (PAS2)	Sorocaba River, downstream of the Ribeirão do Ferro discharge point	23º26'66" S 74º13'599" W
P8 (PAS3)	Sorocaba River, upstream of the Ribeirão do Ferro discharge point, after the Ipanema River discharge point in the Sorocaba River	23º41'69" S 74º14'130" W

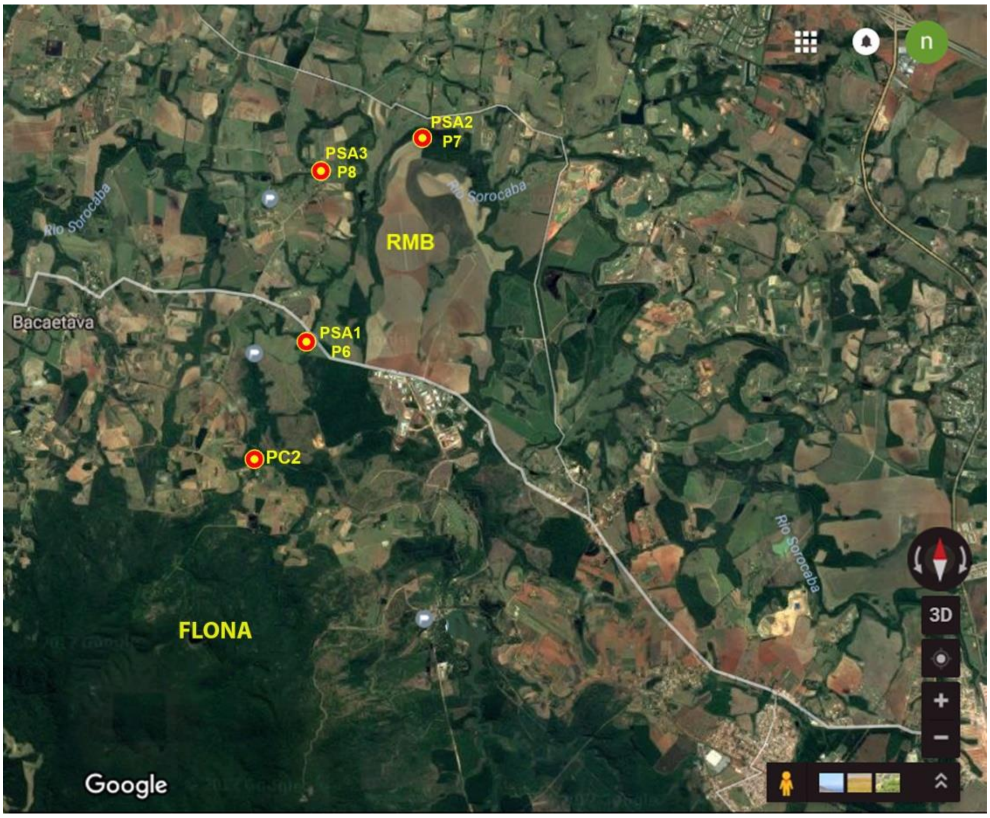

Figure 3: localization of sediment's collection points at study area.

Samples were collected using an *Ekman-Birge* dredge and packed in previously decontaminated and labeled glass containers. After being collected, samples were stored under refrigeration and transported to the laboratories of Centro de Química e Meio Ambiente of IPEN/CNEN-SP, where they were frozen and lyophilized.

2.3. Determination of PAHs

The methods used for the preparation and analysis of PAHs in sediment samples were developed and validated by Brito [3]. To the lyophilized sediment 10 mL of the mixture of acetone and tetrahydrofuran (1:1) added. Then the sample was subjected to ultrasonic bath for 3 hours [3]. The supernatant extract was centrifuged and purified water was added to reach a concentration of tetrahydrofuran/acetone solution about 4:10 of solvent. The diluted extract was percolated in SPE-C18 cartridge (SUPELCO, filled with octadecyl) previously conditioned with 10 mL of purified water followed by 10 mL of purified water/acetone solution 3:10. After percolated of the mentioned diluted extract through the cartridge, a cleanup of column was made with 10 mL of purified water, followed by 5 minutes of vacuum drying and subsequent centrifugation of the cartridge for 25 minutes at 3000 rpm to aid in the elimination of water. The elution of the analytes was made twice with 4 mL (4 x 1 mL) of the tetrahydrofuran/acetone solution (1:1) and then dried in a N_2 smooth flow, taken up to 2 mL of acetonitrile/water (1:1) solution, 0,45 µm membrane filtrate (Millex) and finally analyzed by HPLC.

3. RESULTS AND DISCUSSION

Sediment samples collected during days 19, 20 and 21 in June 2017, rain season, was lyophilized and analyzed according to the methodology described above. The results of the concentrations obtained for each analyzed PAH compound can be observed in Table 4. These results are referent to the collect points previously described in Table 3.

Table 4: Results of the sediment samples analysis collected at 2017 in the studied area.

		PAHs concentration in µg g^{-1}			
Compounds	*LOQ µg g^{-1}*	PC2 2017	PAS1 2017	PAS2 2017	PAS3 2017
Acenaphthylene	*0.030*	< LOQ	< LOQ	< LOQ	0.9±0.2
Fluorene	*0.030*	< LOQ	0.14±0.01	< LOQ	< LOQ
Acenaphthene	*0.016*	< LOQ	0.7±0.1	< LOQ	< LOQ
Phenanthrene	*0.026*	0.05±0.01	0.04±0.01	0.4±0.1	0.10±0.01
Anthracene	*0.036*	< LOQ	< LOQ	< LOQ	< LOQ
Fluoranthene	*0.012*	< LOQ	0.05±0.01	0.21±0.02	0.10±0.01
Pyrene	*0.030*	0.70±0.02	0.35±0.01	1.11±0.03	1.09±0.02
Benzo[a]anthracene	*0.012*	< LOQ	< LOQ	< LOQ	< LOQ
Chrysene	*0.012*	< LOQ	< LOQ	0.080±0.003	0.015±0.001
Benzo[b]fluoranthene	*0.012*	< LOQ	0.017±0.002	0.10±0.02	0.21±0.02
Benzo[k]fluoranthene	*0.016*	< LOQ	< LOQ	0.10±0.02	0.04±0.01
Benzo[a]pyrene	*0.012*	< LOQ	0.030±0.003	< LOQ	0.069±0.003
Dibenzo[a,h]anthracene	*0.040*	< LOQ	< LOQ	< LOQ	< LOQ
Indene[1,2,3-c,d]pyrene	*0.034*	< LOQ	< LOQ	< LOQ	0.040±0.003

LOQ = Limit of Quantify

The obtained results were compared to the Canadian Standard Values for Sediments' Quality (SVSQ), as showed at Table 5. The TEL and PEL reference values are established by the Canadian Council of Ministers of the Environmental, and like the values adopted by CETESB. According to the Canadian legislation, the following limits must be considered: TEL (Threshold Effect Level), which indicates the level below which no adverse effects happens to the biological community; and PEL (Probable Effect Concentration), which is the probable level of the adverse effect to the biological community.

Table 5: TEL and PEL reference values established by the Canadian Council of Ministers of the Environmental, and adopted by CETESB [11].

PAHs	TEL $\mu g\ g^{-1}$	PEL $\mu g\ g^{-1}$
Acenaphthylene	0.006	0.128
Fluorene	-	-
Phenanthrene	0.004	0.515
Anthracene	0.047	0.245
Fluoranthene	0.111	2.355
Pyrene	0.053	0.875
Benzo[a]anthracene	0.032	0.385
Chrysene	0.057	0.862
Benzo[b]fluoranthene	-	-
Benzo[k]fluoranthene	-	-
Benzo[a]pyrene	0.032	0.782
Dibenzo[a,h]anthracene	0.006	0.135
Indene[1,2,3-c,d]pyrene	-	-

Evaluating individual contribution of PAHs in sediment samples, it was observed that the levels of some compounds were above the limits established by Brazilian legislation and the reference values.

Most of the sediments analyzed from four collection points of RMB installation area have so far been exempt or below the limits of quantification for PAHs. However, in some of these collection points, PAHs concentrations were above the TEL and PEL limits and/or CONAMA and CETESB prevention limits [11-12].

According to the results obtained for the PC2 collection point, the compounds Pyrene and Phenanthrene were above TEL limits.

Concentrations at the collection point PAS1 for the Phenanthrene and Pyrene compounds were above the limits of TEL.

At the collection point PAS2 the values obtained for the Phenanthrene, Pyrene, Chrysene and Fluoranthene compounds were above the limits of TEL. The value observed for Pyrene was above the limits of PEL [12].

In the PAS3 sample the Phenanthrene and Benzo[a]pyrene compounds were above the TEL limits and the concentration observed for Acenaphthylene and Pyrene were above the PEL limits [11-12].

Concentrations above the values of TEL and PEL of CONAMA and CETESB may be associated with seasonality. As well as the circulation of automobiles by the road Bacaetava-Sorocaba that directly can influences the pollution of the bodies of water in the vicinity. These trends of increase of PAH concentration were observed in the studies of Brito[13] where it was demonstrated that before the Mario Covas's road ring construction the concentrations were low and after the construction the concentrations increased.

To verify the potential origin of the PAHs, the results were used to calculated ratios between some PAHs, suggested by several literatures to try to identify the sources as burned oil or coal, vehicle emissions and atmospheric transport of pollutants [14-15].

The calculation of the Fluoranthene/Pyrene ratio, at points PAS1, PAS2 and PAS3, can be used to evaluate if the main sources of PAHs studied are pyrogenic [13]. In these points the rate is lower than 1, suggesting that the main source of the studied PAHs is derived from pyrogenic sources, especially from combustion of diesel engines and atmospheric aerosols.

It was observed positive values in two points for Chrysene compound, showed in Table 4. Its occurrence suggest that burning of industrial oil, emission of gasoline combustion gases and incinerators [16]. Associated to Benzo[k]fluoranthene found at points PAS2 and PAS3 (Table 4), could suggest emissions of vehicles, especially diesel [15].

The prevalence of polycyclic aromatic hydrocarbons of pyrogenic origin was observed in sediment samples, associated to the vehicular emissions, the coexistence of other PAHs contamination sources was not observed yet.

4. CONCLUSIONS

These initial results are important to evaluate the concentrations of PAHs before the RMB construction. The results obtained in this study demonstrated that the region is still preserved, but it is necessary to monitor to ensure that the area will not be affected by construction activities.

Sediment can be used as a guide for the assessment of aquatic contamination because it is a compartment of the aquatic ecosystem responsible for the transportation of toxic elements and nutrients and, because it is directly connected to water bodies [17].

The values obtained in this research can be used as guiding values in future works, since there are no previous studies in this region, besides maintaining a periodicity for the verification of environmental impact caused by the construction of the RMB project.

ACKNOWLEDGMENTS

The authors thank to CNPq for a fellowship for this work, to CEN-IPEN, CTM-ARAMAR, CDTN-MG and IRD-RJ.

REFERENCES

1. KUBOTA, L.T.; FREIRE, R.S.; DURÁN, N., ROSATTO, S.S. "Biossensores amperométricos para determinação de compostos fenólicos em amostras de interesse ambiental" *Química Nova*, v. 24, p. 77-86. 2001.

2. LIMA, V. C.; LIMA, M.R.; MELO, V. F. (Eds.) **O solo no meio ambiente**: abordagem para professores do ensino fundamental e médio e alunos do ensino médio. Curitiba: Universidade Federal do Paraná, Departamento de Solos e Engenharia Agrícola, 2007. 130 p.
3. BRITO, C.F. ***Desenvolvimento e validação de metodologia analítica para determinação de hidrocarbonetos policíclicos aromáticos (HPAs) em sedimentos. Avaliação da Represa do Parque Pedroso, Santo André, SP***. Dissertação de Mestrado -IPEN/ USP, 2009.
4. BICUDO, C.E.M.; TUNDISI, J.G.; SCHEUENSTUHL, M.C.B. **Águas do Brasil: análises estratégicas.** São Paulo, SP: Instituto de Botânica, 2010.
5. LEMES, Marcos José de Lima. Avaliação de Metais e Elementos-Traço em Águas e Sedimentos das Bacias Hidrográficas dos Rios Mogi-Guaçu e Pardo, São Paulo. 2001.
6. WHO. *Guidelines for Indoor Air Quality: Selected Pollutants.* Geneva: World Health Organization, 2010.
7. MENZIE CA, POTOCKI BB, SANTODONATO J. Exposure to carcinogenic PAHs in the environment. Environmental Science and Technology. 1992;26:1278–1284.
8. LIOY PJ, et al. The total human environmental exposure study (Thees) for benzo[a]pyrene. Archives of Environmental Health. 1988;43:203–203.
9. MANOLI, E., SAMARA, C. Polycyclic aromatic hydrocarbons in natural water: sources, occurrence and analysis. Trends in Analytical Chemistry. 1999;18:417–428.
10. CHEN HW. Distribution and risk assessment of polycyclic aromatic hydrocarbons in household drinking water. Bulletin of Environmental Contamination and Toxicology. 2007;78:201–205.
11. CETESB Nº 045/2014/E/C/I Valores Orientadores para Solos e Águas Subterrâneas no Estado de São Paulo [Online] // Cetesb. - Fevereiro 20, **2014**. - Fevereiro 12, 2015. - http://www.cetesb.sp.gov.br/userfiles/file/solo/valores-orientadores-2014.pdf.
12. CONAMA - Conselho Nacional do Meio Ambiente - RESOLUÇÃO 357/2005. Ministério do Meio Ambiente. - Março 17, 2005.
13. BRITO, C. F. **Avaliação dos efeitos da construção do rodoanel na qualidade da água e sedimento da represa do Parque Pedroso, Santo André-SP. Estudo geoquímico de hidrocarbonetos policíclicos aromáticos (HPAs), metais e elementos traço com vistas ao abastecimento público.** 2014. Tese (Doutorado em Tecnologia Nuclear - Materiais) - Instituto de Pesquisas Energéticas e Nucleares, Universidade de São Paulo, São Paulo, 2014.
14. SICRE, M. A.; SALIOT, A.; APARICIO, X.; GRIMALT, J.; ALBAIGES, J.; Atmos. Environ. 1987, 21, 2247.
15. VASCONCELLOS, P. C.; ZACARIAS, D.; PIRES, M. A.; POOL, C.; CARVALHO, L. F.; Atmos. Environ. 2003, 37, 3009.
16. FANG, G. C.; WU, Y. S.; CHEN, M. H.; HO, T. T.; HUANG, S. H.; RAU, J. Y.; Atmos. Environ. 2004, 38, 3391
17. QUINÁGLIA, G. A. Caracterização dos Níveis Basais de Concentração de Metais no Sedimento no Sistema Estuário da Baixada Santista. Tese de Doutorado IQ\USP, 2006.